Studies on the Oiliness of Liquids. X. The Friction Coefficients of Mono- and Multi-molecular Layers.*

By Toshizo ISEMURA.

(Received November 22, 1940.)

In one of the preceding papers of this series, the static friction coefficients of glass surfaces on which monomolecular and multimolecular layers of some long chain fatty acids such as palmitic or oleic acid were deposited, had been reported[1]. The friction coefficients of glass surfaces lubricated with such films are about one tenth of that of clean glass. These low friction coefficients were ascribed to the regular arrangement of the molecule. In the present experiment, the friction coefficients of some long chain compounds and cholesterin were measured and the effects of various conditions were also studied.

The friction coefficients were measured by the balance method. The experimental procedure and cleansing of the glass surfaces are quite the same as described in the former papers.[2] The deposition of the monomolecular and multimolecular layers of such long chain compounds on the glass surface were conducted by Langmuir-Blodgett's technique.[3] When no indication is made, tap water was used as the substrate water which was regulated its *p*H value to about 9 by the addition of a small quantity of ammonia. The results are summarized in Table 1. The piston oil used in the deposition of the film is also indicated in the table.

Acids show low friction coefficients, while alcohols show relatively high friction coefficients. Moreover, the values of friction coefficients of alcohols, and ester fluctuate considerably, especially in the cases of tetradecyl and cetyl alcohol. In the table, only the two extreme values were recorded. When the film of long chain acid such as stearic acid was deposited on the glass surface by withdrawal of the glass plate from the water covered with monomolecular film, water is entirely repelled from the glass surface. On the other hand, when the film of alcohol or ester was deposited in the same way, the glass plate was wetted by water. If the glass plate was withdrawn too slowly out of the water surface, the film may slip down from the plate on the water surface. By the withdrawal of the moderate speed the film was transfered on the glass with water and this was dried in desiccator by passing the current of dry air, and used for the friction measurement. By this procedure, the arrangement of the molecules in the deposited film may be irregular. This is a reason of the high friction coefficient and its fluctuation.

The friction coefficient of oleic acid is 0.20 when castor oil was used as the piston oil[1] and somewhat higher than that of elaidic acid. The

* IX, this Bulletin, **15** (1940), 288.

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(1) H. Akamatu and J. Sameshima, this Bulletin, **11** (1936), 791.
(2) J. Sameshima, M. Kidokoro and H. Akamatu, this Bulletin, **11** (1936), 659.
(3) K. Blodgett, *J. Am. Chem. Soc.*, **57** (1935), 1007.

Table 1.

Clean glass: $\mu = 1.04$

Film substance	Piston oil	μ	μ Mean
Elaidic acid	Castor oil	0.10 0.12 0.12 0.13 0.10 0.14 0.10 0.13 0.10	0.12
Myristic acid	Castor oil	0.18 0.20 0.14 0.22 0.18	0.18
	Oleic acid	0.12 0.12	0.12
Linolic acid	Castor oil	0.11 0.15 0.10	0.12
	Oleic acid	0.13 0.09 0.11	0.11
Brassidic acid	Castor oil	0.12	
	Oleic acid	0.11 0.10	0.11
Erucic acid	Castor oil	0.12 0.10 0.11 0.14	0.12
Cerotic acid	Castor oil	0.20 0.13 0.17 0.12	0.16
	Oleic acid	0.17 0.14 0.17	0.16
Triolein	Castor oil	0.20 0.18 0.16 0.17	0.18
Myricyl alcohol	Oleic acid	0.17 0.18 0.19 0.17 0.16	0.17

Table 1.—(*Concluded*)

Film substance	Piston oil	μ	μ Mean
Cholesterin	Castor oil	0.22 0.21 0.21	0.21
	Oleic acid	0.22 0.22	0.22
Tetradecyl alcohol	Castor oil	0.23~0.45	
	Oleic acid	0.19~0.47	
Cetyl alcohol	Castor oil	0.25~0.50	
	Oleic acid	0.18~0.52	
Octadecyl alcohol	Castor oil	0.18~0.34	
	Oleic acid	0.17~0.32	
Methyl palmitate	Castor oil	0.37~0.46	
	Oleic acid	0.32~0.46	

structure of the oleic acid is a cis-form while that of elaidic acid is a trans-form. Elaidic acid can be more closely packed than oleic acid. This fact may be a reason of the different friction coefficients of these two acids which have the same molecular formula. However, brassidic and erucic acid show almost the same friction coefficient. In the films of acids which are solid in ordinary temperature, the arrangement of the molecules is more regular than in that of liquid acids when the films are deposited in compressed state. This fact is a probable reason why oleic acid shows a relatively high friction coefficient. Cholesterin film shows the friction coefficient of the order of that of oleic acid.

In the former communication, it had been also reported that no further reduction of friction coefficient was observed by the increase of thickness of the film. However, in the present experiment it was found that the reduction of friction coefficient is caused definitely by the increase of the thickness of film. The friction coefficient diminishes gradually down to the penta- or heptamolecular layers, and then no further reduction could be recognised. Table 2 and Fig. 1 show the results. Oleic acid is only an exception. This is caused by the liquid nature of the substance in an ordinary temperature. When the number of layers are built up, assemblage of molecules in the film gains gradually the nature of liquid and the orientation of molecules in the film becomes somewhat more ir-

Table 2. μ of multimolecular layers.

Number of layers	Stearic acid	Oleic acid	Brassidic acid	Erucic acid	Palmitic acid
1	0.12	0.14	0.11	0.12	0.10
3	0.09	0.12	0.08	0.08	0.09
5	0.06	0.14	0.07	0.08	0.07
7	0.06	0.15	0.08	—	0.06
9	0.06	0.17	0.08	—	0.06
11	—	—	—	—	0.06

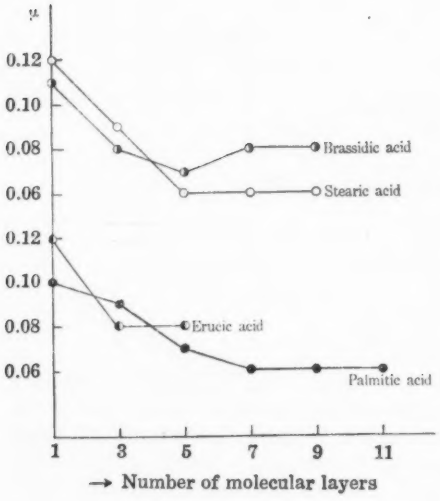

Fig. 1.

regular, so that the friction coefficient of oleic acid increases. Germer and Storks[4] found by the examination of monomolecular and multimolecular layers with electron diffraction that on a clean metal surface molecules of the first layer stand with the axes of the hydrocarbon chains normal to the surface and the chains closely packed together laterally but irregularly arranged whereas in layers on top of the first, molecules of barium sterate or of stearic acid are regularly arranged. Accordingly, the fact that the friction coefficients of multimolecular layers being lower than that of monomolecular layers can be ascribed to more regular arrangement of the molecules in the film.

The effect of compression of the film by some piston oils of different spreading pressures during the deposition of film on the glass is also investigated. The results which were obtained by using oleic acid and castor oil as piston oil are shown partly in Table 1. The low pressure piston oils were prepared according to the indication of Norris and Taylor.[5] The mixtures of various compositions of ethyl myristate and liquid paraffin which was specially purified for this purpose, were used. The spreading pressures were measured by Adam-Jessop's surface balance, and shown in Table 3. With these piston oils the effect of compression were studied. The results are shown in Table 4.

(4) Germer and Storks, *J. Chem. Phys.*, **6** (1938), 280.
(5) Norris and Taylor, *J. Chem. Soc.*, **1938**, 1719.

Table 3.

Piston oil	% of ethyl myristate	Spreading pressure (dyne/cm.)
No. 1	47.2	13.4
No. 2	32.8	10.5
No. 3	18.1	8.2
No. 4	10.1	5.1

Table 4.

Piston oil	Palmitic acid μ	Myristic acid μ
Oleic acid	0.10	0.12
Castor oil	0.11	0.18
No. 1	0.11	0.20
No. 2	0.12	0.18
No. 3	0.13	0.22
No. 4	0.13	0.21

From Table 1 and 4 we see that there occurs, generally, a small change in the values of friction coefficient by changing the piston oils of different spreading pressures. However, the value of μ increases definitely with the decrease of spreading pressure. Relatively large difference of μ was detected with myristic acid. Myristic acid makes an expanded film and the compressibility of the film is larger than the other substances which make the condensed film. In expanded film, molecules arrange rather irregularly even though the film is transferred on the glass plate in compressed state. Myristic acid film may be partly collapsed by the spreading pressure of oleic acid. The film of myristic acid which was deposited in compressed state by oleic acid could not be purely monomolecular.

Subsequently, the effect of the hydrogen ion concentration of the substrate water was investigated. The film transferred from acidic substrate has higher friction coefficient than that transferred from basic substrate. The results are shown in the second column of Table 5. The substrate was distilled water in which barium chloride and potassium bicarbonate were added in the concentration of 10^{-4} mol per litre, and the value of pH was regulated by the addition of ammonia. Stearic acid was used as an film substance. The glass plates on which stearic acid

Table 5.

pH	μ	μ'	% of the fractional conversion to neutral soap
6.50	0.19	0.56	48
6.75	0.16	0.60	54
6.93	0.17	0.54	58
7.39	0.15	0.49	67
8.18	0.12	0.36	80
9.00	0.12	0.24	89
9.26	0.12	0.23	91
9.38	0.12	0.22	92
9.69	0.11	0.16	93

film were deposited by Blodgett's method from the substrate water containing a small quantity of barium ion, were coated by a monomolecular layer consisting of a mixture of stearic acid and barium stearate. These plates were dipped in benzene for about 0.5~1 minute and after withdrawing the plate, the friction coefficients were reinvestigated. It was known that plate coated with the film from basic substrate had relatively low friction coefficient, while the plate coated with the film from acidic substrate had relatively high friction coefficient. According to Langmuir and Schaefer, the film of fatty acid contains metals if the substrate water contains some alkaline earth metals.[6] The films formed by stearic acid are nearly pure neutral soap when the water is strongly alkaline, while they are of free acids when *p*H 3. The ratio of free acids and barium or calcium salts varies according to the values of *p*H. By dipping the plates coated with film in benzene, the free acids may be dissolved whereas the barium salts does not. So that, the friction coefficients of glass surfaces which were covered with the film from acidic substrate, increase considerably by dipping the plate in benzene. However, the plate covered with films from basic substrate show almost the same friction coefficients as before. In the intermediate range of *p*H the friction coefficients change with *p*H. The friction coefficients after dipping in benzene (μ') are shown in the third column of Table 5.

The ratio of barium stearate in the film can be calculated by the experimental formula of Langmuir and Schaefer[6]:

$$\log \frac{f}{f'-f} = -2.41+0.367 \cdot p\mathrm{H}$$

where f denotes the fractional conversion to neutral soap and f' the limiting value of f for high values of *p*H and shown in the fourth column of the table. The friction coefficients decrease almost linear with the ratio of the fractional conversion to neutral soap. Fig. 2 shows the result.

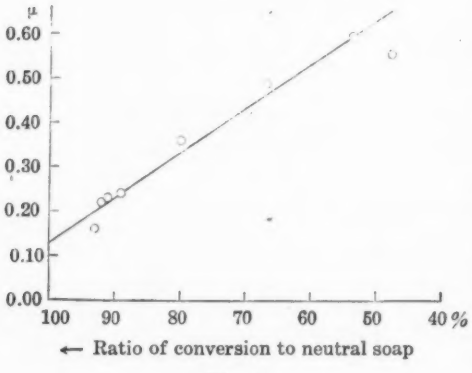

Fig. 2.

In the course of the present experiments, it was experienced that the stearic acid film spread on tap water can be transferred on glass plate more readily than that spread on distilled water only. The force-area relation of the film were studied with stearic acid both on tap water and distilled water using Adam-Jessop's surface balance. The force area curves obtained are reproduced in Fig. 3. It was found that the area occupied by a single molecule is 20.6 sq.

(6) Langmuir and Schasfer, *J. Am. Chem. Soc.*, **58** (1936), 284.

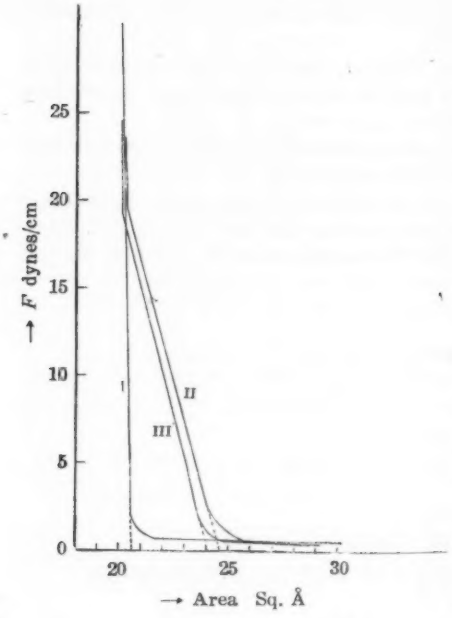

Fig. 3.

Å. on tap water and 24.6 sq. Å. on fresh distilled water. Molecules are more closely packed in the film on tap water than that on distilled water. Molecules in the film on tap water attract each other by lateral forces so that films are stabilised more firmly than the film on distilled water and transferred more readily. On the same reason the films might be deposited on glass plate more readily from basic substrate than from acidic substrate on which molecule occupies larger area.

The effect of the minute amount of metallic ion on the monomolecular films formed by the substance with acidic group was first indicated by Myres and Harkins[7]. The small limiting area of stearic acid on tap water may be ascribed to the effect of the presence of calcium ion in tap water. If ammonium oxalate was added to the tap water in the concentration of 0.05 mol per litre, area per single molecule was increased to 24.1 sq. Å. In Fig. 3, I shows the F-A curve of the stearic acid film on tap water, II that on fresh distilled water and III that on tap water added with ammonium oxalate.

In conclusion, the author expresses his hearty thanks to Prof. J. Sameshima for his kind guidance and encouragement throughout the present work. The expense for the experiments has been defrayed from the grant given to Prof. Sameshima by Nippon Gakujutu Sinkokai (Japan Society for the Promotion of Scientific Research), to which author's thanks are due. The author's acknowledgement is also due to Hattori Hokokai for a grant.

Summary.

(1) The static friction coefficients of glass surfaces covered with the mono- and multi-molecular layers of some long chain acids etc. have been measured.

(2) The friction coefficients of glass covered with monomolecular film of acids are about one tenth of that of clean glass. The friction coefficients of alcohols and esters are somewhat higher but fluctuate considerably.

(7) R. J. Myers and W. D. Harkins, *Nature*, **139** (1937), 368.

(3) The friction coefficients of multimolecular layers decrease by the increase of their thickness until it becomes five or seven molecular layers, but shows no further reduction.

(4) The effect of compression during the deposition of the film was investigated. The film deposited in high compression state shows low friction coefficient.

(5) The film deposited from basic substrate shows lower friction coefficient than that deposited from acidic substrate.

(6) The force area relations of stearic acid monolayer have been studied on fresh distilled water, on tap water, and on tap water added with ammonium oxalate in relation to the transference of the film on the glass plate.

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Polymerisation of Tung Oil. III. Molecular Weights of Tung Oil and its Polymerides.

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The determination of molecular weights of drying oils has the marked importance for the elucidation of polymerisation and oxidation mechanism. However, the results obtained are generally discrepant even with the standard methods. It has been generally known that the molecular weights of fatty oils determined by the cryoscopic method vary to a great extent with the solvent and concentration[1]. As solvent camphor, benzene, nitrobenzene and others are generally used.

The molecular weight to be determined cryoscopically is calculated by the formula: $M=KC/\Delta T$, where K is the calculated depression of the freezing point due to 1 gram molecule of any solute in 100 g. of solution, C the concentration of solute in gram per 100 g. of solution, and ΔT, the observed depression of the freezing point. The molecular weight (which will hereafter be denoted briefly as M) calculated from the above formula is a linear function of concentration (C) in the range of dilute solution.

The true molecular weight corresponding to zero concentration is obtained by extrapolation. But in the case of benzene solution the molecular weight of fatty oils is not a linear function of concentration and the extrapolation to zero concentration is practically impossible.

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(1) Normann, *Chem. Ztg.*, **31** (1907), 211; H. J. Backer, *Chem. Weekblad.*, **12** (1915), 1034; Morrel, *J. Oil Colour Chem. Assoc.*, **7** (1924), 146; Seaton and Sawyer, *J. Ind. Eng. Chem.*, **8** (1916), 490; Rhodes and Welz, *ibid.*, **19** (1927), 68.

Nevertheless the cryoscopic method with benzene is usually preferred, because the operations are easily practicable. J. S. Long and J. G. Smull[2] reported about the oxidation and polymerisation mechanism of linseed oil, using the data of the apparent molecular weight of a constant concentration (molecular weight of 1 g. of oil in 25 c.c. of benzene).

In the study of polymerisation of tung oil, the author reported[3] that the molecular weights of polymerised tung oils calculated from the specific viscosity of benzene solution, when the molecular weight was assumed to be proportional to the specific viscosity, were too great as compared with that inferred from the chemical commonsense. Therefore it is very important to ascertain the relation of molecular weight of polymerised tung oil and the concentration of solution, and to obtain the molecular weight at zero concentration.

Experimentals. Tung oil used was characterized as follows: density (15/15°C.) 0.9409, iodine value (Wijs' method) 166.8, refractive index (n_D^{30}) 1.5164. The polymerised tung oils were obtained by polymerising the raw tung oil at 220°C. and had the following refractive index.

Table 1. Refractive index of polymerised tung oils.

Sample	Polymerisation time (m.)	n_D^{30}
No. 0	Raw oil	1.5164
No. 1	0	1.5122
No. 2	20	1.5109
No. 3	40	1.5097
No. 4	50	1.5090
No. 5	60	1.5082

(1) *Camphor method.* The determination of molecular weight by the melting point depression of camphor was carried out as in the usual method.

For the sake of comparison, the molecular weight of pure oleic acid was measured and the value 290 (calculated molecular weight 284) was obtained. The molecular weight of the polymerised tung oils are shown in table 2.

Table 2. Molecular weights of polymerised tung oils.

Sample	Concentration (%)	Depression of m.p. (ΔT °C.)	Calculated molecular weight
No. 0	4.11	2.25	906
	4.14	2.33	881
	5.01	2.67	931
	5.50	2.80	979
	5.66	3.30	852
	6.17	3.75	810
			893
No. 1	3.35	1.50	1111
	3.68	1.65	1110
	4.77	2.10	1130
	9.97	4.68	(1055)
			1110

(2) J. S. Long and J. G. Smull, *J. Ind. Eng. Chem.*, **17** (1925), 138, 905.
(3) M. Tatimori, this Bulletin, **13** (1938), 142.

Table 2.—(*Concluded*)

Sample	Concentration (%)	Depression of m.p. (ΔT °C.)	Calculated molecular weight
No. 2	4.29	1.68	1269
	4.94	2.00	1230
	5.33	2.50	(1060)
	6.26	2.83	1100
	6.30	2.70	1160
			1220
No. 3	4.42	1.60	1374
	5.28	2.10	1254
	6.50	2.60	1240
	6.63	2.70	(1201)
			1380
No. 4	3.82	1.20	1593
	4.35	1.50	1444
	5.82	1.90	1523
	6.21	2.40	1314
	7.32	3.30	(1140)
			1550

The apparent molecular weight by the camphor method decreases as the concentration increases, but within the range of dilute solution the constant molecular weight is obtained.

(2) *Benzene method.* The molecular weight of oleic acid was measured and the value 565 was obtained. This is twice as much as the theoretical value. The molecular weights of polymerised tung oils are shown in Table 3.

Table 3. Molecular weights of polymerised tung oils.

Sample	Solvent (g.)	Solute (g.)	Concentration (%)	ΔT (°C)	$\frac{\Delta T}{C} \times 10^2$	M
No. 0	17.862	1.145	6.02	0.362	6.01	852
		1.558	8.02	0.530	6.60	795
		1.890	9.57	0.680	7.10	721
No. 1	17.862	0.635	3.44	0.120	3.50	1465
		0.990	5.25	0.200	3.81	1344
		1.521	7.85	0.330	4.21	1217
		2.093	10.49	0.520	4.96	1033
	13.400	2.117	13.64	0.765	5.61	913
		2.368	15.02	0.893	5.95	949
		2.695	16.74	1.035	6.18	817
		3.044	18.52	1.260	6.81	752
No. 2	17.862	1.100	5.80	0.180	3.10	1650
		1.475	7.63	0.259	3.39	1508
		1.820	9.25	0.370	4.00	1280
		2.567	12.56	0.570	4.53	1128
	13.400	1.636	10.88	0.455	4.18	1225
		1.859	12.18	0.588	4.83	1061
		2.209	14.16	0.770	5.44	942
		2.361	14.98	0.840	5.61	913

Table 3.—(*Concluded*)

Sample	Solvent (g.)	Solute (g.)	Concentration (%)	ΔT (°C)	$\frac{\Delta T}{C} \times 10^2$	M
No. 3	17.862	1.202	4.84	0.150	3.10	2152
		1.699	6.67	0.265	3.98	1678
		1.957	7.58	0.320	4.23	1580
		2.500	9.42	0.450	4.78	1396
	13.400	1.812	11.91	0.440	3.69	1387
		2.154	13.85	0.555	4.01	1278
		2.374	15.05	0.645	4.29	1195
		2.528	15.87	0.705	4.44	1153
No. 4	13.400	0.989	6.87	0.148	2.15	2376
		1.415	9.55	0.255	2.67	1916
		1.717	11.36	0.330	2.91	1751
		1.888	12.35	0.385	3.12	1642
No. 5	17.862	1.078	5.69	0.128	2.25	2277
		1.720	8.78	0.203	2.31	2215
		2.203	10.98	0.330	3.01	1703
		2.468	12.14	0.440	3.30	1554
	13.400	2.344	14.89	0.585	3.93	1303
		2.651	16.52	0.710	4.30	1191
		2.743	16.99	0.750	4.41	1159
		2.910	17.88	0.835	4.67	1097

The relations between the apparent molecular weight and the concentration are shown in Fig. 1.

It is noticed that the apparent molecular weight decreases rapidly with increasing concentration. These values, obtained by the camphor method, may be accepted as probable molecular weights. But, for the data obtained in the benzene solution the linear relation does not hold between the apparent molecular weight and the concentration, therefore it is impossible to extrapolate to the zero concentration.

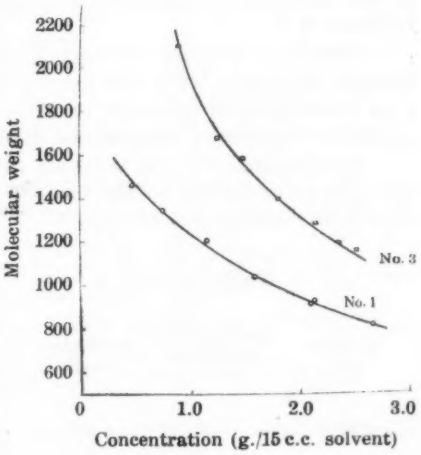

Fig. 1.

A fundamental difficulty in the determination of molecular weights of polymerised tung oil lies in the following fact: in order to increase the accuracy of the measurement, the concentration of the solution must be increased; for this purpose the concentration in weight percent becomes too high, nevertheless the concentration in mol percent remains small, because the molecular weight of polymerised tung oil is very great. This difficulty becomes more eminent as the molecular weight of the solute increases. An abnormally great value for the mole-

cular weight of polymerised tung oil in benzene solution was noticed by Gay[4] and for which he obtained 4320.

This abnormality is probably due to an action between solute and solvent. In other solvents such great values are not obtained. The author carried out the molecular weight determination of another polymerised tung oil, using as solvent nitrobenzene, bromoform and ethylene-bromide. With these solvents the linear function is held between the molecular weight and the concentration, and the values extrapolated to zero concentration are shown in Table 4.

Table 4.

Samples	Heating time at 206 °C. (m.)	n_D^{20}	Nitro-benzene	Bromoform	Ethylene bromide
No. 0	Raw oil	1.5193	800	800	830
1	0	1.5192	820	810	970
2	60	1.5171	960	1120	1160
3	120	1.5149	1320	1360	1420
4	180	1.5139	2095	1785	1940

Thus, reasonable values were obtained.

Gay reported that cyclohexane is an ideal solvent which displays no specific action on the solute. The author determined the molecular weight of raw tung oil in a purified cyclohexane and obtained the results shown in Table 5.

Contrary to other solvents the apparent molecular weight in cyclohexane increases with the increasing concentration and the value at zero concentration amounts to 970. This is a reasonable value for the molecular weight of commercial tung oil.

Discrepancies found between the theoretical value and the observed one may be explained by the mechanism of association of solute, solvation of solvent, association of solvent etc.

Table 5.

Sample (g.)	Melting point depression (ΔT °C.)	Molecular weight
0.3683	0.35	942
0.7721	0.70	1003
1.2168	1.09	1017
1.7161	1.49	1049

Table 6.

Sample	$\lim_{C \to 0} \Delta T/C$	$M_{C \to 0}$	M'
No. 0	4.35	1145	893
1	2.70	1845	1110
2	1.60	3110	1220
3	1.20	4150	1380
4	0.94	5030	1550
5	0.60	8300	—

(4) Gay, *Chemistry and Industry*, **1933**, 70.

It is already known that some of high molecular compounds behave abnormally in the solution[5]. G. V. Schulz and his co-workers[6] tried to obtain reasonable values for the molecular weight by the following formula, $M=RT/\lim_{C\to 0}(P/C)$, where P is the osmotic pressure and C the concentration.

In the case of benzene solution of polymerised tung oils the relation between $\Delta T/C$ and C may approximately be represented by a straight line. Thus the value of $\Delta T/C$ and molecular weight at zero concentration can be calculated as shown in Table 6.

In this table $M_{C\to 0}$ is the molecular weight calculated from $M_{C\to 0}=\frac{k}{100}\left(1/\lim_{C\to 0}\frac{\Delta T}{C}\right)$, and M' the molecular weight determined by the freezing point depression of camphor. Further it is noticed that at the end of cooking the molecular weight of tung oil in benzene solution becomes very great, which coincides with the viscosity data[7].

It is reasonable to think that this abnormality is due to the solvation of benzene. The relation between the molecular weight by camphor and benzene methods is shown in Fig. 2.

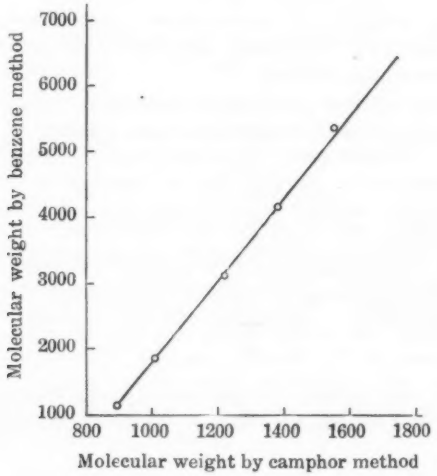

Fig. 2.

An approximate proportionality holds for them. The relations between the molecular weight by camphor method and refractive index, and also heating time of the oil are shown in Figs. 3 and 4.

(5) P. Stamberger and C. M. Blow, *Kautschuk*, **6** (1930), 22.

(6) G. V. Schulz, *Z. Phys. Chem.* B, **196** (1936), 317; G. V. Schulz and H. Staudinger, *Ber.*, **68** (1935), 2320; G. V. Schulz, *Z. angew. Chem.*, **49** (1936), 549.

(7) M. Tatimori, this Bulletin, **13** (1938), 142.

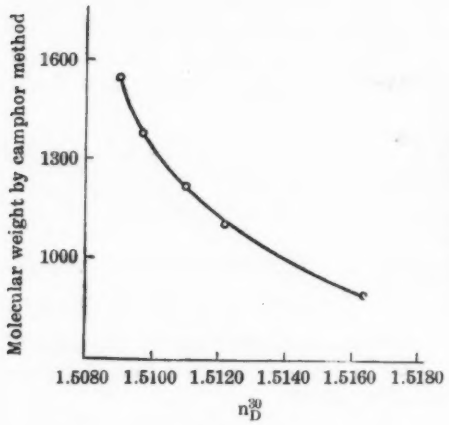

Fig. 3.

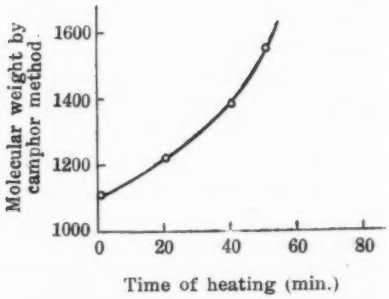

Fig. 4.

Summary.

The molecular weights of polymerised tung oils were measured in the solution of benezne, camphor, nitrobenzene, bromoform, ethylene bromide by the cryoscopic method.

By the camphor method reasonable molecular weights were obtained. But in benzene the molecular weight decreases rapidly with the increasing concentration. In nitrobenzene, ethylene bromide, bromoform the molecular weight behaves as linear function of concentration and the rate of decrease in molecular weight with increasing concentration is not so eminent as in benzene.

On the contrary in cyclohexane the molecular weight increases with the increasing concentration and reasonable values are obtained by extrapolation. The abnormality in benzene may be considered as the solvation action.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Mr. T. Yosioka, and Mr. K. Yokota for their kind guidance.

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On the Metallo-Organic Compounds. X. Electroisomerism in Triethyltin.

By Taichi HARADA.

(Received October 25, 1940.)

The triethyltin group may be prepared in various ways among which the two methods[1),2)]—(1) the reduction of triethyltin halide[1)], or the hydroxide and (2) the oxidation of sodium diethyl stannide or disodium tetraethyl stannide—are shown in equations I and II, respectively. The triethyltin group prepared by the reduction process I and the triethyltin group prepared by the oxidation process II are highly interesting as regards their properties; although of like appearance (their tin content, M.W. in naphthalene and benzene, and refractive index)[1)] their rate of oxidation appears to differ markedly.

$$\text{I.} \quad R_3SnX + Na^+ + \varepsilon^- = R_3Sn + NaX$$

$$\text{II.} \quad R_2Sn^-Na^+ + RX = R_2SnR + NaX \ .$$

The electronic constitutions of the triethyltin groups thus obtained are represented, therefore, as follows:

A. $\begin{matrix} R^- \\ R^- \\ R^- \end{matrix} \!\!\rangle\!\!\!- Sn^{+++}$ B. $\begin{matrix} R^- \\ R^- \end{matrix} \!\!\rangle\!\!\!- Sn^{+++} - R^+$

It is expected from the electronic constitutions that the compound B would be more unstable than the compound A. Such constitutional isomers will be called "electroisomers" by the present author. The stability of the compounds can be determined by their degree of conversion into triethyltin hydroxide or into diethyltin oxide through the formation of triethyltin oxide (b.p. 158°, 15 mm., uncor.,)[1)] in the presene of oxygen and water. At present, under this condition the mechanism of the formation of diethyltin oxide is not known. However, perhaps it would conform with the following equation[3)]

$$\text{III.} \quad R_3SnOH = R_2SnO + RH \ .$$

It cannot be strongly emphasized without further investigation from different points; however the existence of the so-called "electroisomers" is theoretically possible. Table 1, 2 and 3 (corresponding curves in Fig. 1.) illustrate the properties. The boiling points of both samples are approximately the same (152–154°, 17 mm (uncor.) for $(C_2H_5)_3Sn$ and 153–155°, 17 mm (uncor.) for $(C_2H_5)_2SnC_2H_5$).

(1) T. Harada, *Sc. Papers Inst. Phys. Chem. Research* (Tokyo), **35** (1939), 290.
(2) T. Harada, this Bulletin, **4** (1929), 266.
(3) T. Harada, *Sc. Papers Inst. Phys. Chem. Research* (Tokyo), **36** (1936), 501.

Table 1.

A. $(C_2H_5)_3Sn$ 0.4 g. Subs. in 75 c.c. of 75% alc.		B. $(C_2H_5)_2Sn\ C_2H_5$ 0.4 g. Subs. in 75 c.c. of 75% alc.	
Days	*p*H		*p*H
0	6.0		6.2
1	6.6		7.2
3	7.6		7.7
4	7.7		7.7
5	$(C_2H_5)_2SnO = 0.08$ g.		$(C_2H_5)_2SnO = 0.19$ g.

Table 2.

A. $(C_2H_5)_3Sn$ 0.3 g. Subs. in 50 c.c. H_2O			B. $(C_2H_5)_2Sn\ C_2H_5$ 0.3 g. Subs. in 50 c.c. H_2O	
Days	c.c. of $\frac{1}{20}$ N HCl	*p*H	c.c. of $\frac{1}{20}$ N HCl	*p*H
0	0.10	6.9	0.20	7.0
1	0.20	7.1	0.40	7.2
2	0.30	7.2	0.50	7.4
3	0.40	7.3	0.60	7.4
4	0.45	7.4	0.70	7.5
6	0.50	7.4	0.75	7.6
	$(C_2H_5)_2SnO = 0.03$ g.		$(C_2H_5)_2SnO = 0.08$ g.	

Table 3.

A. $(C_2H_5)_3Sn$ 1.0 g. Subs. in 100 c.c. H_2O			B. $(C_2H_5)_2Sn\ C_2H_5$ 1.0 g. Subs. in 100 c.c. H_2O	
Days	c.c. of $\frac{1}{20}$ N HCl	*p*H	c.c. of $\frac{1}{20}$ N HCl	*p*H
0	0.05	6.7	0.05	6.8
1	0.08	6.8	0.10	7.0
2	0.15	7.0	0.20	7.1
4	0.20	7.1	0.35	7.2
6	0.25	7.2	0.45	7.4
8	0.30	7.3	0.55	7.5
11	0.40	7.4	0.65	7.5
14	0.50	7.5	0.75	7.6
16	0.55	7.5	0.75	7.6
18	0.60	7.5	0.75	7.6
21	0.65	7.6	0.80	7.6
24	0.70	7.6	0.80	7.6
29	0.70	7.6	0.80	7.6
	$(C_2H_5)_2SnO = 0.10$ g.		$(C_2H_5)_2SnO = 0.27$ g.	

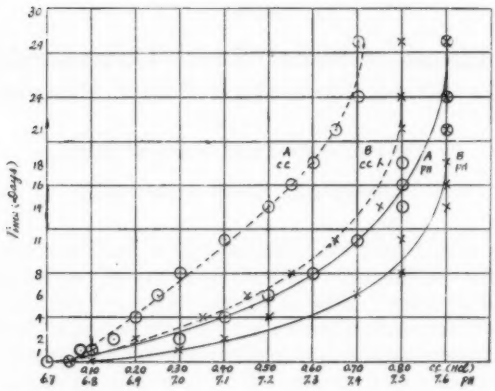

Fig. 1.

Experimental. One gram of sample A and B prepared by equations I and II respectively (and purified by distillation, and washing with alcohol and water)[1] were covered with 100 c.c. of water in Erlenmeyer flasks and agitated occasionally in a similar manner. One c.c. of each of the clear top aqueous solution was taken out and diluted with 10 c.c. of water, and finally was titrated with $\frac{1}{20}$ NHCl using methyl orange as indicator. Ten c.c. of the diluted solution were determined for *p*H simultaneously with phenol red as indicator. Insoluble $(C_2H_5)_2SnO$ on the other hand, was also formed by the above treatment. A similar experiment was also carried out with 0.4 g. of each of the sample but they were covered with 75 c.c. of 75% alcohol instead of water. The titration and the determination of *p*H were carried out similarly as above but for *p*H below 7.0, bromothymol blue was employed as indicator. In both cases, the total amount of diethyltin oxide precipitated from $(C_2H_5)_2SnC_2H_5$ was approximately three times that from $(C_2H_5)_3Sn$.

Summary.

The free triethyltin groups prepared by two methods, namely, the reduction of $(C_2H_5)_3SnX$ and the oxidation of $(C_2H_5)_2SnNa$ or $((C_2H_5)_2SnNa)_2$ appear to be identical. However, their rate of oxidation appears to differs markedly from one another. It is assumed that this is due to their electronic constitutional difference (electroisomeric) or in the methods of preparation.

The author wishes to express his appreciation to Dr. T. Suzuki for his kind advice during this investigation.

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Antioxygenic Effects of Some Nitroso Compounds. An Interpretation of the Effects from the Point of View of Resonance.

By Yojiro TSUZUKI and Yukio KIMURA.

(Received November 30, 1940.)

It was shown by Carré and Peigné[1] that antioxygenic action seems to depend on the difference of the polarity of elements directly to antioxygenic substances. The authors have now examined several nitroso compounds for antioxygenic activity on the autoxidation of benzaldehyde exposed to atmospheric oxygen, since nitroso compounds have, in general, very large dipole moment. Their antioxygenic actions are, however, somewhat diverse. Some are very effective and some are not.[2] Aliphatic nitroso compounds (such as nitroso-dimethylamine and nitroso-methylurethane) generally show no or very little retarding effect, while aromatic compounds show more or less strong activity.

Some examples of our experiments using nitrosobenzene, *p*-nitroso-toluene, *p*-chloro-, *p*-bromo- and *p*-iodo-nitrosobenzenes as antioxidants will be shown.

In a flask of 1370 c.c. volume, 5 c.c. freshly distilled benzaldehyde (5×10^{-2} mols) and the antioxidant (4×10^{-5} mols) are introduced. After standing for 24 hours the formed benzoic acid is titrated with alkali.

Antioxidant	Benzoic acid formed	Antioxidant	Benzoid acid formed
None	1.263 g.	*p*-Chloro-nitrosobenzene	0.074 g.
Nitrosobenzene	0.777 g.	*p*-Bromo-nitrosobenzene	0.069 g.
p-Nitrosotoluene	0.599 g.	*p*-Iodo-nitrosobenzene	0.018 g.

The experiments show that the order of the effects of the substituents is $I>Br>Cl>CH_3>H$. This order is just coincident with the sequence of the *o,p*-directive forces of groups in aromatic substitution,[3] which may be regarded as being determined by the electromeric effect of the radicals.[4] The above results, therefore, indicates that the antioxygenic activity is likely to depend on the resonance of a nitroso compound, which is effected easily in the presence of conjugated double bonds as in the cases of aromatic nitroso compounds.

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(1) P. Carré and L. Peigné, *Compt. rend.*, **208** (1939), 108.

(2) Among nitroso compounds the following ones have been already examined on the autoxidation of benzaldehyde with the results: nitroso-methylurethane is almost inactive, but *p*-nitroso-dimethyl-aniline is very active. C. Moureu, C. Dufraisse and M. Badoche, *Compt. rend.*, **183** (1926), 823.

(3) A. F. Holleman, *Chem. Rev.*, **1** (1925), 187.

(4) On the electromeric effect of the methyl group see E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, **1940**, 949.

Geochemische Untersuchungen der Vulkane in Japan. XXIV. Radongehalt von Mineralwasser in Masutomi.

Von Shinya OANA und Kazuo KURODA.

(Eingegangen am 22. November 1940.)

Bekanntlich gibt es in Masutomi, Kai-Provinz, stark radioaktive Mineralwasserquellen und die Untersuchung über ihren Radongehalt wurde schon früh im Jahre 1914 von R. Ishizu ausgeführt.(1) Neuerdings wurden die gleichartige Messungen von Radongehalt und weiter die Radiumbestimmung in dem genannten Mineralwasser von T. Nakai im Oktober, 1936 und im April, 1937 wiederum geleistet und berichtet.(2)

Wir haben gelegentlich der Studienreisen nach Masutomi im Juli, 1939 und im Oktober, 1940 die Radonbestimmungen derselben Quellen nochmals durchgeführt, um kennen zu lernen, ob der Radongehalt solcher Quellen mit den Zeiten etwaige Veränderung erleide oder nicht. Die Resultate unserer Messungen werden in Tabelle 1 angegeben.

Tabelle 1. Radongehalt von Mineralwasser in Masutomi.

	Namen der Quelle nach Nakai	Juli 1939			Oktober 1940		
		Radon in 1 L. Wasser, in Macheeinheit	Temp. der Quelle °C.	*p*H-Wert	Radon in 1 L. Wasser, in Macheeinheit	Temp. der Quelle °C.	*p*H-Wert
A_1	Kinsentō	2.06	31.0	6.3	1.44	31.6	6.2
A_2	Tuganerō No. 1	4.3	30.1	6.4	4.21	32.3	6.3
A_3	,, No. 2	3.45	29.6	6.4	2.62	30.7	6.5
A_4	Totikubo No. 1	16.1	28.0	6.3	4.24	27.5	6.3
A_5	Hiuke-sui		14.7			13.5	6.0
B_1	Nibuzawa		24.0			24.2	6.6
B_2	Sio-no-sawa-tugane-yu		20.9			19.0	6.0
B_3	Gantō-hunsen		26.0			16.5	6.2
B_4	Kuridaira No. 1		21.2	6.0	638	22.3	5.9
B_5	Kuridaira-tennen-buro		23.6	6.4	4.78	21.3	6.5
B_6	Kuridaira No. 3	233	21.4		258	20.0	6.0
B_7	Higasiobi-no-izumi	9.05	24.5	6.3	9.02	25.0	6.3
B_8	Wadegawara No. 1		22.0	6.5	675	19.0	6.5
B_9	,, No. 2	1090	20.5	6.2	1200	18.8	6.0
C_1	Ginsentō-kami-no-yu		28.5	6.5	30.3	25.9	6.9
C_2	Ginsentō-huru-yu		30.0	6.5	132	31.3	6.5

(1) R. Ishizu, "The Mineral Springs of Japan," 85, (1915).
(2) T. Nakai, dies Bulletin, **15** (1940), 363.

Tabelle 1.—(*Fortsetzung*)

	Namen der Quelle nach Nakai	Juli 1939			Oktober 1940		
		Radon in 1 L. Wasser, in Macheeinheit	Temp. der Quelle °C.	*p*H-Wert	Radon in 1 L. Wasser, in Macheeinheit	Temp. der Quelle °C.	*p*H-Wert
C_3	Ginsentō-naka-no-yu		27.0	6.7	31.8	21.9	6.7
C_4	Ginsentō-simo-no-yu				228	19.4	6.4
C_5	Ōsiba		22.6	6.4	419	23.2	6.4
C_6			29.1	6.6	17.2	22.0	6.5
D_1			11.3	3.8		11.2	3.7
D_2	Yuzawa No. 5		14.7	5.4		12.0	5.4
D_3	,, No. 4		11.8	3.8		11.2	3.8
D_4	,, No. 3		11.9	4.0			
D_5			14.1	4.0			
D_6			14.4	5.8	2.64	14.0	5.6
D_7	Yuzawa No. 1		17.8	6.0	2.76	18.0	5.6
D_8			18.0	5.9			
D_9			15.5	5.5			
D_{10}			14.0	3.7			
D_{11}			16.5	5.6			
D_{12}			16.1	5.5			
E	Wada-matuba-Kōsen		11.5	6.4	3.48	12.5	6.5

Wir haben alle Mineralwasserquellen in Masutomi in 5 Gruppen geordnet, die in der Tabelle mit den Buchstaben A, B, C, D und E bezeichnet sind. Die angehängten Ziffern bedeuten die Stellen der Quellen, die in Reihenfolge nach der Höhe auf die Meeresfläche angeordnet sind. Die von T. Nakai gegebenen örtlichen Bezeichnungen[2] sind in zweiter Reihe der Tabelle angegeben und sie beziehen sich auf unsere Zeichen in erster Reihe.

Was die Diskussion über jetzt von uns erhaltene Resultate anbelangt, so möchten wir sie bis zur folgenden Mitteilung, die bald zur Erscheinung kommen wird, hinhalten.

Es sei uns gestattet, Herrn Prof. Yuji Shibata und Herrn Prof. Kenjiro Kimura für ihre freundliche Anleitung und Ratschläge, und der Kaiserlichen Akademie der Wissenschaft für ihre finanzielle Unterstützung bei der Ausführung dieser Arbeit unseren herzlichen Dank auszusprechen.

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CORRECTIONS.

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Page	Line	
95	6	*for* "the" *read* "a"
,,	Table 1	*for* "2:1 (26.0) or (1:1)*", "m:n" *read* "2:1 (26.0) or 1:1*", "1:1?"
96	Table 2	*for* "*m*-Bromobeezene" *read* "*m*-Nitrobromobenzene"
97	1 and 2	insert "2:1 naphthalene—styphnic acid;"
,,	Fig. 2, Foot-note	*for* "Date", "obtained in" *read* "Data", "obtained from"
99	9 from bottom	*for* "on" *read* "in"
,,	Foot-note (14)	*for* "C. Shinomiya" *read* "T. Asahina and C. Shinomiya"
100	17	*for* "74.0" *read* "76.5"
,,	18	*for* "76.5" *read* "74.0"
,,	20	*for* "43.0 35.6 28.3" *read* "57.0 64.4 71.7"
,,	Foot-note (17)	*for* "moles %" *read* "mol %"
103	3 from bottom	*for* "Hattori-Hokakai" *read* "Hattori-Hokokai"
140	3 and 4	*for* "gas(3)", "ring(4)" *read* "gas(4)", "ring(5)"
142	Fig. 3	*for* "α-Naphthol" *read* "α-Naphthylamine"
143	27	*for* "24.0 mol %" *read* "22.8 mol %"
261	2 and 8	*for* "methyderivatives" *read* "methyl derivatives", "combine" *read* "combines"
,,	Table 2, Foot-note	*for* "V" *read* "∨"
262	Table 3, left 18	*for* "1:1 (–3.2)" *read* "1:1 (–3?)"
,,	,, , right 9	*for* "$C_6H_4 \cdot CH_3 \cdot NO_2$ 1,2" *read* "$C_6H_4 \cdot CH_3 \cdot NO_2$ 1,3"
265	10	*for* "picramide" *read* "pyrene"
,,	6 from bottom	*for* "(*w*)" *read* "(ω)"
266	5	*for* "trinitrotoluene" *read* "pyrene"
269	26	*for* "75.0" *read* "87.0"
,,	27	*for* "87.0" *read* "75.0"
282	5 in Table 1	*for* "1:1 [190.5]* 81.5" *read* "1:1* [190.5] 81.5"